APPENDIX A:

Information on Work Group's Determination that More HAP Emissions Data are Necessary to Support the ICCR Rule Development

The RICE Work Group has concluded that additional emissions data are necessary to support the ICCR rule development. This conclusion was reached as a result of the Work Group's review of emissions data available to the ICCR process in the EPA ICCR Emissions Database for RICE.

The RICE Work Group established the Emissions Subgroup in February 1997 to review the emissions data in the EPA ICCR Emissions Database for RICE. Members of the Subgroup reviewed the emissions test reports that were the source of the ICCR emissions data for RICE.

In March 1997, the Subgroup reported on the results of their review. The Subgroup noted that the emission levels reported in the ICCR Emissions Database for RICE were highly variable. The Subgroup speculated that the variability could be attributed to two possible causes:

1. reported formaldehyde levels in some cases may be artificially low due to interference with DNPH-based test methods, and
2. emissions may be affected by the operating condition of the engine when tested.

When the Subgroup reviewed the test reports to determine if the variability could be explained by the operating conditions of the engines, the Subgroup discovered that many of the test reports lacked key information about engineering and operating parameters that could affect HAP emissions. For example, the manufacturer and model of the engine were often lacking in test reports. Whether the engine was a 2-stroke or 4-stroke cycle was lacking. The air-to-fuel ratio was often lacking, as was the horsepower and speed (rated and as tested). The Subgroup concluded that there was insufficient information in the test reports to account for the unexplained variability in the emissions data included in the ICCR Emissions Database for RICE. The Subgroup also concluded that, apparently, there is no existing data for testing a single engine over the entire envelope of operating conditions.

The RICE Work Group has not made a final decision on the use of data in the ICCR Emissions Database for RICE – some of the data may be useful in the ICCR process, while, clearly, some of the data will be inadequate for use in ICCR. However, the RICE Work Group has identified key emissions data gaps, including the following:

1. the effect of operating conditions on emissions, and
2. the effectiveness of possible MACT control devices in reducing HAP emissions.

EPA also has noted the deficiencies in the ICCR Emissions Database for possible MACT control devices. In an October 1, 1997 memorandum to the Emissions Subgroup, Amanda Agnew of EPA notes that although there is some data in the database for before and after controls, the data for NSCR "correspond to a limited number of pollutants and high detection limits (FTIR with a 0.5 ppm detection limit)," and the data for oxidation catalysts have the following limitations, "1) the unavailability of emission data necessary to estimate a representative control efficiency, and 2) only a small portion of the pollutants were measured before and after controls."

Given the critical data gaps, the RICE Work Group agreed, by consensus, that additional emissions data are needed to support the ICCR rule development.

APPENDIX B:
Background Information on Engines and Emission Controls

1.0 Engines to be Tested

1.1 Types of Engines

Stationary reciprocating internal combustion engines come in a wide variety of makes and models utilizing both liquid and gaseous fuels in diverse applications. The various types can be described according to:

operating cycle
scavenging cycle
fuel type

A brief description of each of these categories is provided below.

1.1.1 Operating Cycle

There are two operating cycles in common use for reciprocating internal combustion engines: spark ignition (SI), also known as otto cycle, and compression ignition (CI) also known as the diesel cycle. The SI cycle uses lower compression ratios than does the CI cycle and relies on a mechanical spark to ignite the fuel mixture in the cylinder. The CI cycle uses high compression and the resultant high temperatures to effect auto-ignition of the fuel in the cylinder. The intake process for both SI and CI cycles, including the fuel mixing process and ignition timing, impacts the initiation and the rate of combustion, which, in turn, may impact air toxics formation. A more detailed description of both operating cycles is provided below.

1.1.1.1 Spark Ignition (SI)

SI engines utilize a "spark" generated by a spark plug and associated electronics to initiate combustion. Traditionally, one or more of these spark plugs were mounted directly in the combustion chamber. While simple, when applied to larger bore engines, such "Open Combustion Chamber" (SI-OCC) systems result in significant combustion instability and can operate only at moderately lean air/fuel ratios. To extend the lean limit (and thereby reduce NO_x emissions while improving efficiency) Original Engine Manufacturers (OEMs) introduced two-stage combustion including a rich initial phase that has sufficient energy to light off the very lean secondary phase. Usually the rich phase is ignited by the spark in a "Pre-Combustion Chamber" (SI-PCC).

Recently, several after-market manufacturers have offered alternative electrical based ignition systems such as plasma jets. Typically these High-Energy (HE) ignition systems operate in an OCC, and will be referred to as HE-OCC in this document.

1.1.1.2 Compression Ignition (CI)

Compression Ignition engines operate at significantly higher compression ratios than SI engines, with the resultant heat of compression raising the temperature of the trapped air or air/fuel charge to ≈800°F or more. Fuel (usually liquid) injected into this hot compressed gas then spontaneously vaporizes, disassociates and ignites. Often CI engines are referred to as "diesel" engines after the originator and patent holder of the method[1]. While some vehicular diesel engines utilize a pre combustion chamber to assist in ignition, particularly at part load, all large stationary CI "diesels" have OCCs to maximize efficiency and performance.

The other major type of CI engine scavenges or injects gaseous fuels into the combustion chamber with the fresh air charge and then utilizes a small "pilot injection" of liquid fuel (usually No. 2D) to ignite the mixture. Typically called "dual fuel" or "gas-diesel" engines, the less expensive gaseous fuel usually provides 90-99% of the input energy while the more expensive liquid fuel provides the balance. Originally, dual fuel engines were simple conversions of OCC diesel engines which maintained the ability to operate on "full diesel" (i.e. 100% liquid fuel). While offering favorable NO_x emissions in this configuration (4-5 g/BHP-HR), subsequent regulatory pressure to further reduce emissions resulted in several OEMs offering such engines fitted with PCCs to reduce the pilot fraction to ≈1% or less.

By their nature (i.e. ignition via heat of compression), all stationary CI engines are inherently "lean burn", usually utilizing turbochargers and intercoolers to achieve the desired fresh air density.

1.1.2 Scavenging Cycles

Reciprocating internal combustion engines utilize either 2-stroke cycle (2SC) or 4-stroke cycle (4SC) scavenging. The efficacy of the scavenging cycle will impact the trapped air/fuel charge in turn impacting air toxics formation. A summary of the various scavenging cycles and equipment configurations is provided below.

1.1.2.1 4-Stroke Cycle

4SC are the most familiar engine type due to their use in vehicular applications. A 4SC engine undergoes four distinct events or "strokes". Each cycle consists of; intake, compression, power and exhaust. Due to the pumping action of the intake and exhaust strokes, 4SC engines are self-aspirating or "scavenging"[2]. 4SC engines operating at

[1] Rudolph Diesel originally wanted to utilize coal dust as the fuel but soon changed to liquid fuels when the former burned uncontrollably and proved excessively abrasive.

[2] The word scavenge in this use refers to the removal of spent exhaust gases and their replenishment with a fresh air charge.

fresh air charge densities induced only by this inherent pumping action are often referred to as Naturally Aspirated (NA). Inasmuch as maximum power delivery is limited by the air supply, 4SC NA engines tend to operate near or slightly rich of stoichiometry, hence the appellation "rich burn".

In general, financial and performance considerations require that large (>500 BHP) stationary 4 SC engines operate at specific outputs 2-4 times that obtainable with NA alone. Therefore these engines utilize an auxiliary air compressor to increase the charge density at the engine intake. The most common method is to utilize an exhaust-gas-driven turbine to drive the compressor, usually called a "turbocharger". In addition, to maximize the fresh air charge density, most 4SC turbocharged (4 SC TC) engines utilize an aftercooler or intercooler to remove the heat of compression from the fresh air charge. Typically, mechanical and/or thermal loading limits the output of 4SC TC engines. 4 SC TC engines can operate from rich of stoichiometry to more than twice as lean as stoichiometry (over 100% excess combustion air). A common method used to differentiate between “rich burn” and “lean burn” engines is with percentage oxygen in the exhaust stream. Several regulatory agencies have adopted a value of 4% oxygen in the exhaust as the defining limit for “rich burn” engines. An engine with more than 4% exhaust oxygen is classified as “lean burn”. In point of fact, most “lean burn” engines manufactured today contain at least 7% exhaust oxygen.

1.1.2.2 2-Stroke Cycle

To maximize power output/density, 2SC engines eliminate the intake and exhaust "pumping" strokes of 4SC engines, retaining only the compression and power strokes. Consequently, an auxiliary device is required to "scavenge" the engine. In their simplest form this may consist of pumping off the underside of the piston or the addition of one or more scavenging pump cylinders to the same crankshaft connecting the power cylinders. In more sophisticated applications gear or motor driven blowers may supply scavenging air. Typically, due to inherent limitations in 2SC scavenging, these pump scavenged (2SC PS) or blower scavenged (2SC BS) 2SC engines operate somewhat lean of stoichiometric and are also classified as "lean burn".

Like 4SC, financial and performance considerations (in particular the parasitic load of crank driven pumps/blowers), require that larger more modern stationary 2 SC engines utilize turbochargers and intercoolers to increase charge air density and hence specific output. 2SC TC engines typically operate lean of stoichiometric conditions and therefore, are known as lean-burn engines.

1.1.3 Fuel Type

Fuel type and associated mixing impact initiation, rate and completeness of combustion, which in turn impacts air toxics formation. Stationary internal combustion engines utilize either liquid or gaseous fuels.

1.1.3.1. Liquid Fuels

With the exception of extremely small co-generation applications (≈<100 kW) liquid fueled SI engines are seldom utilized in stationary applications. Rather, all stationary liquid fueled engines operate on the CI cycle. However, due to the simplicity and robustness of this ignition method, CI engines can operate on a wide variety of liquid fuels ranging from light distillates such as No. 2 fuel oil to residuals from the refining process which are virtually solid at room temperature, sometimes called residual or "heavy" fuel.

1.1.3.2 Gaseous Fuels

Most stationary SI engines operate on gaseous fuels while many stationary CI engines utilize gaseous fuels as the primary energy input. In both cases, most engines use either field or pipeline-quality Natural Gas (NG).

A number of SI and CI engines, usually in "co-generation" applications, operate on other gaseous fuels typically the by-product of some unrelated process. These include "Digester Gas" (DG) from the treatment of wastewater, "Process Gas" (PG) from chemical refining processes and "Landfill Gas" (LFG) from solid waste in landfills.

1.2 Driven Equipment

While the driven equipment generally does not impact air toxics formation per se, the driven equipment does affect the operating speed and torque profile. In particular, operation at high speeds and low torque may encourage air toxics formation while reduced speed and high torque operation can reduce air toxics formation.

1.2.1 Reciprocating compressors

Probably the most common application of stationary engines, engine driven reciprocating compressors are utilized in the "Oil & Gas" industry to gather and process natural gas and in the "Natural Gas Pipeline" to transport natural gas to end users. Typically these engines operate over a range of varying speed (≈80-100% of rated) and torque (≈90-120%). Depending on various parametric settings (i.e. air/fuel, ignition timing, etc.) over the operable range of speed and torque, air toxics formation could vary considerably. Therefore air toxics testing of engines driving reciprocating compressors should minimally include the four speed/torque corners (i.e. max speed/max torque, min speed/min torque, etc.).

1.2.2 Generators

The next most common application, synchronous AC generators driven by stationary engines, is utilized to:

- provide prime power in remote locations (i.e. Hawaii, Alaska, etc.)

- provide peak/municipal power to the local grid in populated areas
- "co-generate" power in conjunction with waste heat recovery with the possibility to provide excess power to the local grid in populated areas
- provide emergency power for hospitals, airports, data centers, nuclear power plants, and other facilities.

AC generator drives must operate at fixed (synchronous) speed. Therefore, only the torque varies, typically over the range of 75-100% of rated. Other than air/fuel ratio and spark timing on gaseous-fueled engines, parametric variation tends to be limited. Air toxics emissions should be tested at minimum and maximum torque and at possible timing extremes.

1.2.3 Miscellaneous

After reciprocating compressors and generators, most remaining stationary engines drive rotating compressors, blowers, pumps etc. In general, these machines follow a quadratic relationship between speed and torque (i.e. the torque absorbed is proportional to the square of the speed). Worst case air toxics formation should generally occur at either the minimum or maximum normal operating speed.

2.0 Emission Control Devices to be Tested

In general, emissions control strategies for stationary internal combustion engines focus on NO_x reduction, either by altering the combustion process or exhaust after-treatment. None of these strategies currently focus on the formation/reduction of air toxics.

2.1 Altered Combustion Process

Most larger "lean burn" stationary reciprocating engines subject to emissions limitations utilize some form of altered combustion process to reduce NO_x emissions, which could also impact (most likely increasing) the formation of air toxics. This usually includes parametric adjustments to lean out the air/fuel mixture, often in conjunction with PCCs on SI engines to obtain minimum NO_x. Other NO_x reducing parametric adjustments include retarded injection or ignition timing and reduced charge temperatures.

A few engines may employ other forms of combustion modification including Exhaust Gas Recirculation (EGR) or Water Injection (WI), the latter on diesels only.

2.2 Exhaust After-Treatment

In some applications, stationary reciprocating engines may utilize exhaust gas after-treatment to reduce emissions, again primarily NO_x. This generally consists of a catalytic device.

The three principal catalyst technologies that have been applied to stationary IC engines are:

1) Selective catalytic reduction, (SCR) - which injects a "reducing agent" (typically ammonia, NH_3) into the exhaust stream upstream of the catalyst to "extract oxygen" from NOx compounds, transforming them into molecular nitrogen, N_2.

2) Non-selective catalytic reduction, (NSCR) - is used on “rich-burn” engines that can operate at approximately stoichiometric (chemically correct) air/fuel ratios. NSCR catalysts rely on the engine to produce sufficient carbon monoxide (CO) to act as a reducing agent to extract oxygen from the NOx compounds. Maintaining the proper CO/NOx ratio for proper operation requires very precise air/fuel control.

3) Oxidation catalysts - are used on lean burn engines to reduce the CO that is formed as a product of partial combustion in very lean engines.

The primary HAPs constituent from natural gas engines is formaldehyde, CH_2O, which is formed when conditions do not allow methane to oxidize completely. Formaldehyde is a product of partial combustion, as is CO. The removal of formaldehyde requires the use of a catalyst that promotes further oxidation. SCR catalysts are not expected to be effective in reducing formaldehyde since they are formulated to enhance reduction reactions only. NSCR catalysts are formulated to enhance both reduction and oxidation reactions. It is therefore expected that both NSCR and oxidation catalysts will exhibit some effectiveness in oxidizing formaldehyde. This has been confirmed in the limited field testing that has been conducted to date.

NSCR catalysts appear to be particularly effective for two reasons: 1) engines operating with stoichiometric air/fuel ratios operate with particularly high in-cylinder temperatures which tend to destroy formaldehyde in the combustion chamber, and 2) engines operating at stoichiometric conditions have hot exhaust temperatures which keeps the catalyst in its optimum temperature range for high efficiency. The combination of low “engine-out” HAPs emissions (although NOx levels are high for stoichiometric operation) and high catalyst efficiency should combine to produce effective oxidation of formaldehyde. NSCR catalysts are the most common catalysts for stationary engines, and are applied primarily for NOx control.

The application of oxidation catalysts is less common, but they are used when CO levels from lean burn engines must be reduced. Lean burn engines can have high specific emissions of formaldehyde due to the cool combustion process and a high degree of flame quenching in the cylinder. Unfortunately, the cool combustion temperatures, which tend to raise formaldehyde levels, can also suppress catalyst efficiency. The exhaust stream of a lean burn engine is colder than that of a “rich-burn” (approximately stoichiometric) engine; this suppresses the efficiency of the catalyst. One of the most challenging applications will be for lean-burn two-stroke cycles, which utilize large amounts of scavenging air. High scavenging rates can drastically reduce the exhaust temperatures. The cool exhaust / catalyst temperatures are expected to make the lean-burn 2-stroke cycle engine the most difficult application. Oxidation catalysts in use have primarily been formulated for oxidation of CO, and have not been optimized for oxidizing formaldehyde or other hydrocarbons. It has been shown that oxidation catalysts can be applied to lean-burn engines to reduce formaldehyde, but do not produce the high reduction efficiencies seen with NSCR catalysts on rich-burn engines due to the differences in exhaust temperatures. If an NSCR catalyst is used on a lean-burn engine, it will promote oxidation, but will have very poor NOx reduction efficiency. Oxidation catalysts are preferred over NSCR catalysts for lean-burn engines.

The efficiency of catalytic after-treatment controls on air toxics is uncertain. In some situations beneficial oxidation of air toxics may occur. However, before and after testing is necessary for verification.

APPENDIX C:
Engine Set Up, Execution of Test Runs, and Data Acquisition

1.0 Roles / Responsibilities

Relevant roles during the test include the following:

Test Director

The Test Director will be an engine expert approved by the RICE Work Group. The test director will coordinate all aspects of the test including engine operation, analyzer operation and calibration and assessment of the stability and suitability of engine performance. The test director will review and define required engine maintenance, tuning or adjustment and convey those requests to the Plant Liaison. The test director will elect when to start and stop the test runs and then assess the suitability of each individual run. The test director will generate, review and distribute all final Test Condition Summary Data Sheets and associated archives.

Performance Analyst

The performance analyst will perform analysis of the power cylinder balance and combustion stability and the compressor cylinder horsepower as requested by the test director. The analyst will also assist plant staff in balancing of the power cylinders and diagnosis of any combustion performance aberrations.

RM Operator

The RM operator will maintain and operate all criteria analyzers and related equipment up to and including the stack probe. The RM operator will coordinate pre and post test calibrations with the test director. The RM operator will also perform all post test drift correction calculations and provide the test director with all final drift corrected emissions values.

FTIR Operator

The FTIR operator will maintain and operate the FTIR and all related equipment after the stack probe. The FTIR operator will coordinate pre and post test calibrations with the test director. The FTIR operator will also perform all post test drift correction calculations and provide the test director with all final drift corrected emissions values.

Plant Liaison

Provided by the host company, the plant liaison will coordinate engine loading with gas control, direct the plant operators to set the engine to the desired condition, and arrange for the execution of any maintenance requested by the test director. The plant liaison is responsible for ensuring the engine and auxiliaries operate in a safe manner that will not compromise their life or operability or endanger the test team.

2.0 Engine Set Up and Testing Conditions

2.1 Pre-test Preparation

At the beginning of each test day, the RM & FTIR operators will perform preliminary calibration of their instruments. The plant liaison will arrange for the calibration of all engine sensors as requested by the test director. The test director will walk down the engine and all systems with the plant liaison to ensure the unit is properly prepared for testing.

2.2 Engine Set-up

Prior to establishing a new test condition, the test director will review the desired test condition with the plant liaison, who in turn will coordinate setting of the engine and auxiliaries to the desired condition.

The test director will then monitor engine operating and emissions parameters and assess stability and suitability of engine performance. The test director will define any required special engine adjustments and, when satisfied, direct the performance analyst to collect a set of readings. Reviewing the results, the director will define any required corrective action. Once satisfied, the test director will begin preparations for a test run.

2.3. Test Run

Once satisfied with the engine set-up, and confident the engine is operating at steady state at the desired condition, the test director will notify the RM and FTIR operators to perform calibrations (as required). Once complete, the test director will begin collecting 10-minute data sets with the DBDAQ, monitoring engine performance and engine speed and load stability throughout. The director will continue to collect data sets until at least three satisfactory runs are obtained at the desired test condition. Upon completion of all runs for a given condition (or as required) the test director will notify the RM and FTIR operators to perform post-calibrations (as required) to reestablish drift correction factors.

Upon completion of each test condition, the test director will generate and distribute a preliminary Test Condition Summary Data Sheet. At the end of each day, the RM and FTIR operators will generate final drift corrected emissions values which the test director will then incorporate in the final Test Condition Summary Data Sheet.

2.4 Initial Baseline Testing

2.4.1 Engine Preparation, Instrumentation Setup, Calibration and Validation

Prior to initiation of the testing, confirm all scheduled maintenance for the engine and auxiliaries is up to date. Confirm that the engine is in a reasonable, repeatable state of health and tune consistent with good operating practices. Pay particular attention to the condition of the ignition/injection system. Install new spark plugs, replace or rebuild pre-combustion chamber check valves, clean and pop test fuel injector nozzles, etc., as applicable. All engine adjustments, ignition/injection timing, fuel system, air system, etc., should be set per the manufacturer's specifications.

Any additional sensors that are required for the testing must be installed. Calibrate all sensors providing engine control, performance and emissions parameter sensors. Confirm proper indication of each sensor value at the DBDAQ.

Start and operate the engine at rated speed and torque. Monitor all engine control, performance and emissions parameter sensor values and confirm credibility/validity. Perform hand calculations and cross checks of all calculated parameters such as fuel flow, BHP, BSFC, exhaust flow, emissions mass rates, etc. Take corrective action as required.

2.4.2 Engine Control System Shakedown

Operate the engine at various extremes of operation, including the four corners of the torque / speed map as defined in the matrix of operating conditions.

At each condition, monitor the various control, performance and emissions parameters including speed, intake manifold temperature, intake manifold pressure, IWT, jacket water temperature, fuel flow, exhaust O2, and others specified by the RICE Work Group. Confirm that the automation can control the engine over the operating range with sufficient stability (commonly defined as an acceptable tolerance of speed and/or load variation around the desired mean values) to obtain repeatable data. Investigate and resolve any instabilities, inconsistencies, problems, etc.

2.4.3 Engine Performance Repeatability Test

Operate the engine in stable conditions at rated speed and torque (baseline condition). Collect three or more test runs. Disturb the engine by altering one or more control parameters and operate at that condition for at least one hour. Return the unit to rated speed and torque. Once equilibrium is obtained, collect three or more test runs. Repeat the baseline test for each day of testing and compare to the initially defined baseline runs. Determine overall non-repeatability in baseline operation and determine typical variations in control, performance and emissions parameter values.

3.0 Exhaust Sampling System Description

Specific protocols for sample collection will be submitted to the IC Engine Work Group for review and approval prior to testing. In general, the samples will be collected as described below.

3.1 Criteria Pollutant Reference Method System

Reference Method (RM) trailers will draw an exhaust sample via a probe installed downstream of the turbochargers if so equipped. The conditioned sample will then pass through a common manifold to criteria pollutant analyzers. Each analyzer will output a signal to a Data Acquisition System (RMDAQ) which will correct the data for drift and calculate mass and brake-specific emissions rates. The RMDAQ also will continuously hand the emissions analyzer data off to the database data acquisition system (DBDAQ).

3.2 HAPs FTIR System

HAPs FTIR trailers will draw exhaust from a train probe mounted adjacent to the RM probe. The sample is passed through the FTIR. The FTIR DAQ will perform the necessary Fourier analyses and then determine and display/archive/print the resultant emissions. The FTIR DAQ also will continuously hand the emissions data off to the DBDAQ.

4.0 Data Collection

Specific protocols for collecting engine parameter data, emissions data, and specifications for the data acquisition systems will be submitted to the IC Engine Work Group for review and approval prior to testing. Fuel analysis will be conducted for all emissions tests. In general, engine parameter data must meet the minimum requirements specified below.

4.1 Hardware Description

Must be able to pull all engine operating parameters as well as emissions (criteria and HAPs) into a common database (DBDAQ). May or may not be separate data acquisition system.

4.2 Emissions Data

Data on criteria and HAP pollutants must be supplied to a central data acquisition system.

4.3 Engine Operating and Performance Parameters

The minimum data that will be transmitted to the DBDAQ includes:

Engine Speed
Engine Torque or Load
Spark or Injection Timing
Intake Manifold Pressure (IMP)
Intake Manifold Temperature (IMT)
Fuel Flow Rate
Air Flow Rate
Exhaust Manifold Temperature (upstream of TC if so equipped)
Jacket Water Temperature (JWT)

Other data may include:

Intercooler Water Temperature (IWT) if so equipped
Inlet Air Temperature (ambient)
Inlet Air Pressure (ambient barometer)
Ambient Humidity
Exhaust Manifold Pressure
Turbocharger Speed

In addition, the following data will be recorded where available and/or applicable:

Average peak combustion pressure
Location of peak combustion pressure
Standard deviation of the peak combustion pressure
Individual cylinder exhaust temperatures

4.4 Data Reduction

During actual testing, the DBDAQ will scan all inputs at a rate of 1 Hz and perform all relevant calculations continuously, including:

Fuel Flow
Exhaust Flow (O_2 Balance)
Exhaust Flow (C Balance)
Air Flow
Air/Fuel Ratio
F/A Equivalence Ratio
Brake Specific Fuel Consumption (BSFC)
Emissions Mass Rates (NO_x, CO, THC & HAPs)
Brake Specific Emissions Rate (NO_x, CO, THC, & HAPs)

Upon successful completion of each test run, the test director will archive the data on the DBDAQ hard drive, import the data into a preliminary Test Condition Summary Data Sheet and print a preliminary copy of the data for review and comparison with other test runs.

APPENDIX D:
Response to Comments Received on Pollutant Lists

1.0 Lists of Pollutants Presented at the July Coordinating Committee Meeting

The lists of the pollutants proposed by the RICE Work Group for the purpose of emissions testing are provided below. The RICE Work Group has not yet determined which pollutants may be regulated for RICE under ICCR.

Diesel Fuel (for emissions testing only)

1. 1,3-Butadiene
2. Acetaldehyde
3. Acrolein
4. Benzene
5. Beryllium
6. Cadmium
7. Chromium
8. Ethylbenzene
9. Formaldehyde
10. Hexane
11. Lead
12. Manganese
13. Mercury
14. Naphthalene
15. Nickel
16. POMs (PAHs)
17. Selenium
18. Toluene
19. Xylene

Digester Gas (for emissions testing only)

1. 1,4-Dichlorobenzene(p)
2. Acetaldehyde
3. Acrolein
4. Benzene
5. Ethylbenzene
6. Formaldehyde
7. Methylene Chloride
8. Styrene
9. Toluene
10. Vinyl Chloride
11. Xylene

Landfill Gas (for emissions testing only)

1. Acetaldehyde
2. Acrolein
3. Benzene

4. Carbon Tetrachloride
5. Chloroform
6. Ethylbenzene
7. Formaldehyde
8. Methyl Chloroform (1,1,1-Trichloroethane)
9. Tetrachloroethylene (Perchloroethylene)
10. Toluene
11. Trichloroethylene
12. Vinyl Chloride
13. Xylene

Natural Gas (for emissions testing only)
1. 1,1,2,2-Tetrachloroethane
2. 1,3-Butadiene
3. Acetaldehyde
4. Acrolein
5. Benzene
6. Chlorobenzene
7. Ethylbenzene
8. Ethyl Chloride (Chloroethane)
9. Formaldehyde
10. Methylene Chloride
11. Naphthalene
12. POMs (PAHs)
13. Toluene
14. Xylene

Propane (for emissions testing only)
1. Acetaldehyde
2. Acrolein
3. Benzene
4. Ethylbenzene
5. Formaldehyde
6. Naphthalene
7. Toluene
8. Xylene

2.0 Request For Input On Pollutants To Be Tested

In response to comments received at the July Coordinating Committee meeting, the Reciprocating Internal Combustion Engine (RICE) Work Group accepted recommendations for additional pollutants which should be included in plans for future emissions testing of internal combustion engines under ICCR.

3.0 Comments Received on Pollutants To Be Tested and Work Group Responses

Seven comments were received from members of ICCR outside the RICE Work Group in response to the Work Group's request for input on the pollutant lists. In addition, the Coordinating Committee recommended that the Work Group consider dioxin, based on the information included in the Dioxin Primer. The comments and the Work Group's responses are provided below.

COMMENT #1

From: Richard Van Frank, INTERNET:vanfrank@iquest.net

Date: 8/2/97 9:35 PM

RE: Hg-landfill gas

Sender: vanfrank@iquest.net

This is one reference to Hg in landfill gas; one that the EPA should have known about. There are many other references to this in the literature.

Determination of Landfill Gas Composition and Pollutant Emission Rates at Fresh Kills Landfill-Project Data (on diskette)

Summary:
Air emissions of landfill gas pollutants at Fresh Kills Landfill, located in Staten Island, NY, were estimated based on three weeks of sampling of flow, concentration, and flux at passive vents, gas extraction wells, gas collection plant headers, and the landfill surface conducted by Radian Corporation in 1995. Emission rates were estimated for 202 pollutants, including hydrogen sulfide, mercury vapor, speciated volatile organic compounds, methane, and carbon dioxide. Results indicate that large amounts of mercury enter the methane recovery plant. Emission factors based on the results are presented.

Additional information:
Format: Diskette. The datafile is on one 3 1/2 inch DOS diskette, 1.44M high density.
This product contains text only. Customers must provide their own search and retrieval software.

Work Group Response

Mercury was not added to the list of pollutants to be tested. No engines using landfill gas will be tested as a part of this test plan. Also, review of the data cited revealed extremely low mercury emissions from the entire landfill, 2.3 pounds per year.

The Fresh Kills is the largest landfill in the US, over 3,000 acres, located on Staten Island. The landfill processes 13,000 tons / day. Initial testing of the landfill indicated that mercury emissions were .00545 g/sec. This corresponds to 378 pounds/yr. The mercury measurements were performed using a portable analyzer rather than the standard EPA reference method.
The results were noted as being particularly high, which raised more questions about the testing methodology. A follow-on study was commissioned to examine the mercury emissions in more depth, using EPA reference methods. The follow-up test showed much lower mercury emissions, a total of 2.3 lb/yr from the entire landfill.

COMMENT #2

Date: August 1, 1997
From: Tom McGrath, Energy and Environmental Research Corporation

I attended the ICCR Coordinating Committee Meting in Long Beach, CA on July 23 including the RICE work group presentation of "Pollutants Identified for Emissions Testing Under ICCR." I also attended the ICCR Testing and Monitoring Protocol work group meeting on July 25 and expressed some comments regarding the RICE work group presentation. The ICCR Testing and Monitoring Protocol work group suggested I send my comments directly to you. These comments are:

1. The proposed lists of HAPs to be included in Test Plans for IC engines firing the fuels natural gas and diesel are well supported by the existing HAPs emissions data. My understanding from the Coordinating Committee meeting is that someone is to investigate which HAPs may be formed under combustion conditions based on the composition of inlet streams and combustion chemistry. You may want to consult this "potential HAPs" list prior to finalizing the HAPs lists for natural gas and diesel fuel (and all other fuels).

2. This comment references the Table from the presentation entitled "Pollutants Reported as "Detects"." Seven HAPs were measured during the single propane test reported and all seven HAPs were detected. Nine HAPs were measured during the single landfill gas test reported and all nine HAPs were detected. These data suggest other HAPs, which were not measured, may be present in the exhaust of IC engines firing these fuels. Propane and landfill gas are more complex fuels than natural gas. It therefore follows that HAPs emissions from IC engines firing propane and landfill gas will be at least as great as HAPs emissions from IC engines firing natural gas. This suggests that the propane and landfill gas HAPs list should include all HAPs detected in the exhausts of IC engines firing natural gas.

3. It is expected that landfill gases contain organo-chlorines from the breakdown of municipal waste. Emissions of chlorinated HAPs from landfill gas combustion in IC engines are therefore possible either as uncombusted landfill gas constituents or as products of incomplete combustion. This suggests the landfill gas HAPs list should include the chlorinated HAPs species that have been detected in other tests and/or listed in the "potential HAPs" list referenced in Comment 1.

4. 1,4-Dichlorobenzene(p) was measured in the exhaust of IC engines firing digester gas. Measurements of chlorobenzene were not made. The formation of chlorobenzene only requires the extraction of one chlorine atom from 1,4-Dichlorobenzene(p). The presence of 1,4-Dichlorobenzene(p) suggests chlorobenzene should be measured during future tests.

5. Naphthalene was detected in the exhaust of IC engines firing propane and is included in the Table from the presentation titled "Proposed Pollutants for Emissions Tests Under ICCR". Naphthalene is the lightest polycyclic aromatic hydrocarbon (PAH) and is likely a building block for heavier PAH. This suggests PAH measurements should be included in the IC engines tests firing propane.

6. Please note that the additional target HAPs suggested in this correspondence do not necessarily require additional test methods and testing costs. Most of the additional HAPs suggested in this correspondence can be measured by the methods that will be required to measure the HAPs listed in the Table from the presentation titled "Proposed Pollutants for Emissions Tests Under ICCR".

Please contact me at (714) 552-1803 if you have questions or require clarification of these comments.

Work Group Response

1. The list of "potential HAPs" developed by the Testing and Monitoring Protocol Work Group has been compared to the lists of pollutants for diesel fuel and natural gas. If the Coordinating Committee prepares another list of potential HAPs, the RICE Work Group will compare the lists of pollutants to be tested to that list, to determine if any pollutants should be added to the testing program.
2. The list of HAPs for natural gas has been compared with the lists for other fuels.

    For digester gas, 1,3-butadiene, naphthalene, and PAHs are the only pollutants on the natural gas list (save the chlorinated compounds, which were reported for natural gas apparently as a result of field contamination of the samples, see Work Group Response to Comment #6) that are not on the digester gas list. 1,3-butadiene was tested for RICE using digester gas multiple times (see ICCR Emissions Database for RICE) and was never detected. If no 1,3-butadiene is present, it is reasonable to assume there is no naphthalene or PAHs present.

    For diesel, all the HAPs included on the natural gas list are on the diesel fuel list, save the chlorinated compounds. Since the chlorinated compounds apparently were reported for natural gas as a result of field contamination of the samples (see Work Group Response to Comment #6), no additional pollutants have been added for diesel fuel.

For landfill gas, 1,3-butadiene, naphthalene, and PAHs are the only pollutants on the natural gas list (save the chlorinated compounds, see Work Group Response to Comment #6) that are not on the landfill list. There are no tests for these compounds in the ICCR Emissions Database for RICE. These compounds will be added to the pollutant list for landfill gas.

For propane, 1,3-butadiene and PAHs are the only pollutants on the natural gas list (save the chlorinated compounds, see Work Group Response to Comment #6) that are not on the propane list. Since Naphthalene was detected for propane, it is reasonable to assume that 1,3-butadiene and PAHs may be present. These compounds will be added to the pollutant list for propane.

3. The chlorinated compounds reported in the ICCR Emissions Database for fuels other than landfill gas are 1,1,2,2-tetrachloroethane, chlorobenzene, ethyl chloride, methylene chloride, 1,4-dichlorobenzene(p), and vinyl chloride. These compounds will be added to the pollutant list for landfill gas.
4. RICE Work Group stakeholders familiar with digester gas indicate that chlorobenzene has been tested for RICE using digester gas and is reported 9 times out of 10 as a non-detect. Chlorobenzene will not be added to the pollutant list for digester gas.
5. Since Naphthalene was detected, it is reasonable to assume PAHs may be present. PAHs will be added to the pollutant list for propane.
6. The Work Group agrees that the additional HAPs can be quantified with the test methods proposed under this Test Plan, for little, if any, additional cost.

COMMENT #3

Date: Thu, 21 Aug 1997 13:01:08 -0500
From: "William O'Sullivan" <WOSULLIV@dep.state.nj.us

As discussed at the last Coordinating Committee meeting, testing should include the following:

1. CO, particulates and NOx - These criteria pollutants are important in order to better correlate toxic emissions with combustion conditions. Sometimes high organic HAPS are simply the result of poor combustion, which can be best recognized from high CO levels. Correlation of low HAPs with low CO may lead to use of CO limits and monitoring as MACT for organic HAPs. NOx is needed to weigh the environmental consequences of combustion conditions that may increase NOx, but decrease HAPs and CO. Particulates are needed for the same reason; that is we may need to weigh NOx increases against CO, HAP and particulate decreases in some cases. Also, the coordinating committee may want to recommend NOx, particulate,

and CO control measures; along with HAP control measures.

2. The fuels should be tested for at least the inorganic HAPs which are likely to be in these fuels, including mercury. Where the inorganic HAP is likely not to be caught by an air pollution control device, then fuel testing for the HAP is sufficient. Mercury will fall into this category for most units. Some of the stack testing for the other inorganic metals might be deleted and replaced with fuel testing results where it is expected that most of the metal will be emitted because there is no particulate control device on the unit.

Work Group Response

1. Criteria pollutants, including CO, PM, NOx, and THC will be measured simultaneously with the HAP measurements.

2. Fuel testing for metals in diesel fuel has been added to the Test Plan, in lieu of stack measurements for metals.

COMMENT #4

"Jeffrey.Shumaker@ipaper.com [SMTP:Jeffrey.Shumaker on 08/20/97 12:02:00 PM

To: Sam Clowney
cc:
Subject: Re: Request for Input on Pollutants to be Tested for RICE

I submit for your consideration the idea of sampling for methanol from digester gas combustion. I'm not sure what materials are digested in the units fueling IC engines, but methanol is clearly an issue in the digestion of wood to produce paper fiber and I presume it could be an issue with other cellulose-containing biomass. For example, methanol is the primary indicator HAP in the MACT for pulp mills.

I am not suggesting that methanol is a dangerous HAP. In fact, we have a petition pending at EPA to remove methanol from the HAP list altogether. However, if it is present in quantity, it could be an indicator of proper combustion.

It may well be that I'm off-base given the digestion process(es) you are working with and I'm not suggesting that I or the industry I represent feels testing of methanol is important or even known to be warranted. I simply wanted to bring this potential issue to your attention.

Work Group Response

RICE Work Group Stakeholders familiar with RICE using digester gas reviewed this issue. Orange County tested for methanol in 1995 and no methanol was detected in any test. Methanol will not be added to the pollutant list for digester gas.

COMMENT #5

Date: Wed, 27 Aug 1997 15:58:18 -0400
From: Michael Wax <mwax@icac.com
Reply-To: mwax@icac.com
Organization: Institute of Clean Air Companies
To: jsnyder@alpha-gamma.com
Subject: Your Message of August 20

Based on elementary combustion chemistry, any compounds found in the exhaust of natural gas-fired engines also is very likely to be found in the exhaust of digester gas-, landfill gas-, and propane-fired engines. Therefore, I suggest adding all of the natural gas compounds listed, with the possible exception of the chlorinated compounds, to the other lists.

Work Group Response

The Work Group reviewed the list of pollutants reported for natural gas, save the chlorinated compounds (see Work Group Response to Comment #6). The results of this comparison are summarized under Work Group Response to Comment #2.

COMMENT #6

FROM: Michael J. Atherton, Columbia Gas

SUBJECT: RICE Work Group, Request for Additional Pollutants for Emissions Testing

This Group identified 14 hazardous air pollutants that should be included in plans for future testing of natural gas reciprocating engines. The list includes 4 chlorinated hydrocarbons (1,1,2,2 - Tetrachloroethane, chlorobenzene, ethyl chloride and methylene chloride). The chlorination of alkanes requires chlorine (Cl_2) and a temperature at 250 - 400° C; the chlorination of benzene requires Cl_2 and $FeCl_3$; the chlorination of alkenes requires the presence of Cl_2 and the reaction is usually carried out in an inert solvent such as carbon tetrachloride; alkenes can also be chlorinated using hydrochloric acid, the first step being the transfer of hydrogen in the HCl to the alkene molecule. Since natural gas does not contain Cl_2 or HCl, these chlorinated compounds will not be formed during combustion and there is no reason to include these compounds in the list. These reactions are discussed in any introductory course in organic chemistry.

Small quantities of chloride ion (Cl^-) from produced water may be entrained in the natural gas but cannot result in the production of chlorinated hydrocarbons. The mechanisms require either Cl_2 or HCl.

Work Group Response:

The RICE Work Group requested that Dr. Laura Kinner of Emissions Monitoring, Incorporated, review the two test reports in the ICCR Emissions Database that report quantities of chlorinated compounds for natural gas sources. Dr. Kinner's findings, provided below, indicate that there is evidence of field contamination of the exhaust samples. The Work Group concludes that the compounds were not present in the exhaust, but were introduced by contamination during the sample collection process. Therefore, the chlorinated compounds have been removed from the pollutant list for natural gas.

Summary of Dr. Kinner's findings:

Chlorinated volatile organic compounds were reported in natural gas-fired reciprocating engine effluent at concentration levels in the low parts per billion. The chlorine source for the thermal formation of these compounds is unknown; however, the fuel source is not suspected by industry representatives to contribute chlorine for these reactions.

The test methods used during the two subject field tests at natural gas-fired reciprocating engines were SW846 - 0030 (VOST) and Method TO - 14. The VOST method employs a combination of Tenax and Tenax and activated charcoal adsorbent traps as sample collection media. Analysis is accomplished by thermal desorption of the traps onto a separate Tenax trap, followed by desorption onto a GC column. Detection of the compounds is accomplished by a mass spectrometer. Method TO - 14 employs an evacuated SUMMA canister to withdraw sample gas from the source. The gas sample is analyzed by adsorption onto a Tenax trap or cryogenically cooled trap, followed by desorption onto a GC column. Detection of the compounds is accomplished by a mass spectrometer. Because a mass spectrometer is a specific detector, it is unlikely that the chlorinated volatile organic compounds that were detected were misidentified.

Contamination of various sample collection and analysis media by volatile organic compounds is encountered frequently in practice, and is difficult and sometimes impossible to eliminate. Compounds such as toluene, methylene chloride, carbon tetrachloride and trichloroethane are common laboratory solvents that frequently are detected in method blank samples because of their ubiquitous use as laboratory and field sample recovery solvents. It is postulated that the source of the volatile chlorinated compounds detected in the natural gas-fired effluent is derived from low concentration level contamination of the sample collection and analysis media by laboratory solvents, or possibly carryover from other testing projects.

Examination of both subject reports reveals the following information. One report contains data indicating low concentration levels of chlorobenzene, chloroethane, 1,1-dichloroethane and tetrachloroethane collected by the VOST method. It is unclear from the report whether any chlorinated volatile organic compounds were detected in the field and laboratory blank samples during this testing program. Therefore, the level of potential field or laboratory contamination can not be assessed. The second report employing Method TO - 14 contains data for numerous organic compounds collected from five natural gas-fired reciprocating engines. Almost every TO - 14 field sample reports data for chlorinated compounds, specifically methylene chloride and trichlorethane. Data from laboratory blank samples show no evidence of contamination; however, the field blank samples contained substantial levels of methylene chloride and trichlorethane relative to those levels reported in actual effluent samples. The field blank data are limited to only two samples collected during the testing project duration; however they support the hypothesis that the natural gas-fired effluent is not the source of chlorinated volatile organic compounds.

COMMENT #7

FROM: Lee Gilmer

Subject: Engine Testing HAPs list

Comment A:
We have some questions/concerns regarding the subject list.
Specifically:
* Diesel Fuel - We question the inclusion of beryllium, cadmium, and chromium. Is there actual data (not below detection limit values) that suggest these compounds are present in diesel exhaust? If not, what is the basis for including them? If so, is it reasonable to expect these compounds to really be present?
* Natural gas - We question the inclusion of 1,1,2,2-tetrachlorethane, chlorobenzene, ethyl chloride (chloroethane), methylene chloride, and 1,3-butadiene. Same questions as above. Also, is there data that conclusively attributes any of these compounds to transmission gas as opposed to raw gas? Can you explain why some of the lighter organics even if present in the fuel wouldn't be destroyed in the combustion process?

Comment B: I just happened to notice a bottle of methylene chloride sitting on a table in one of our labs where GC analyses are performed. This jogged my memory that various solvents including methylene chloride are used in analytical labs. I'm pretty sure the only way methylene chloride can be measured in engine exhaust samples is to use an analytical device which just may happen to use some laboratory equipment that may have been exposed to methylene chloride. I have confirmed this with members of the ICCR Testing and Monitoring Workgroup. I believe it would be a travesty if somehow/someway ICCR regulations were developed on HAPs that showed up in testing reports due to such testing artifacts.

Work Group Response

Comment A: Fuel testing for metals has been adopted as a part of the RICE Test Plan in lieu of stack testing for metals (see Work Group Response to Comment #3). The chlorinated compounds have been removed from the list of pollutants to be tested for natural gas as a result of Dr. Kinner's finding that the chlorine was introduced as a contaminant during the sample collection process in the field (see Work Group Response to Comment #6).

Comment B: Methylene chloride is used commonly in laboratories and often can be a contaminant. Based on Dr. Kinner's review of the test reports, there is evidence that the chlorine reported for natural gas-fired engines was introduced as a contaminant during the sample collection process in the field (see Work Group Response to Comment #6).

COORDINATING COMMITTEE GUIDANCE ON DIOXIN

The CC requests that the Work Groups consider the content of the dioxin primer presentation in their deliberations; and when applicable, that consideration be given to good combustion practices (GCP) including pollution prevention, control device efficiencies, and surrogate pollutant levels in addition to existing data sets.

Work Group Response

The Work Group has determined that dioxin will not be included on the list of pollutants for reciprocating internal combustion engines. The Work Group chose not to include dioxin based on consideration of the content of the dioxin primer, including the low to moderate priority assigned to testing for dioxins from reciprocating internal combustion engines.

4.0 Revised Lists of Pollutants to be Tested

The revised lists of the HAP pollutants to be tested are provided below. Please note that these lists were developed for the purpose of emissions testing only. The RICE Work Group has not yet determined which pollutants may be regulated for RICE under ICCR.

Diesel Fuel (for emissions testing only)
1. 1,3-Butadiene

2. Acetaldehyde
3. Acrolein
4. Benzene
5. Beryllium
6. Cadmium
7. Chromium
8. Ethylbenzene
9. Formaldehyde
10. Hexane
11. Lead
12. Manganese
13. Mercury
14. Naphthalene
15. Nickel
16. POMs (PAHs)
17. Selenium
18. Toluene
19. Xylene

Digester Gas (for emissions testing only)
1. 1,4-Dichlorobenzene(p)
2. Acetaldehyde
3. Acrolein
4. Benzene
5. Ethylbenzene
6. Formaldehyde
7. Methylene Chloride
8. Styrene
9. Toluene
10. Vinyl Chloride
11. Xylene

Landfill Gas (for emissions testing only)
1. Acetaldehyde
2. Acrolein
3. Benzene
4. Carbon Tetrachloride
5. Chloroform
6. Ethylbenzene
7. Formaldehyde
8. Methyl Chloroform (1,1,1-Trichloroethane)
9. Tetrachloroethylene (Perchloroethylene)
10. Toluene
11. Trichloroethylene

12. Vinyl Chloride
13. Xylene
14. 1,3-Butadiene (new)
15. Naphthalene (new)
16. POMs (PAHs) (new)
17. 1,2,3,3-Tetrachloroethane (new)
18. Chlorobenzene (new)
19. Ethyl Chloride (new)
20. Methylene Chloride (new)
21. 1,4-Dichlorobenzene(p) (new)
22. Vinyl Chloride (new)

Natural Gas (for emissions testing only)
1. 1,3-Butadiene
2. Acetaldehyde
3. Acrolein
4. Benzene
5. Ethylbenzene
6. Formaldehyde
7. Naphthalene
8. POMs (PAHs)
9. Toluene
10. Xylene

Propane (for emissions testing only)
1. Acetaldehyde
2. Acrolein
3. Benzene
4. Ethylbenzene
5. Formaldehyde
6. Naphthalene
7. Toluene
8. Xylene
9. 1,3-butadiene (new)
10. POMs (PAHs) (new)

APPENDIX E:
Estimated Costs to Conduct RICE Emissions Testing

The RICE Work Group requested assistance from the Testing and Monitoring Protocol Work Group to estimate the costs to perform the emissions testing outlined in this Test Plan. The Testing and Monitoring Work Group estimated that the four emissions tests proposed, data analysis, and data reporting would cost **$610,000**, assuming that the test sites are located in “reasonably accessible locations.”